CHROMIUM CONTAMINATION IN ARMY FACE MASKS

NATIONAL RESEARCH COUNCIL
WASHINGTON, DC

1989

19970521 095

DTIC QUALITY INSPECTED 1
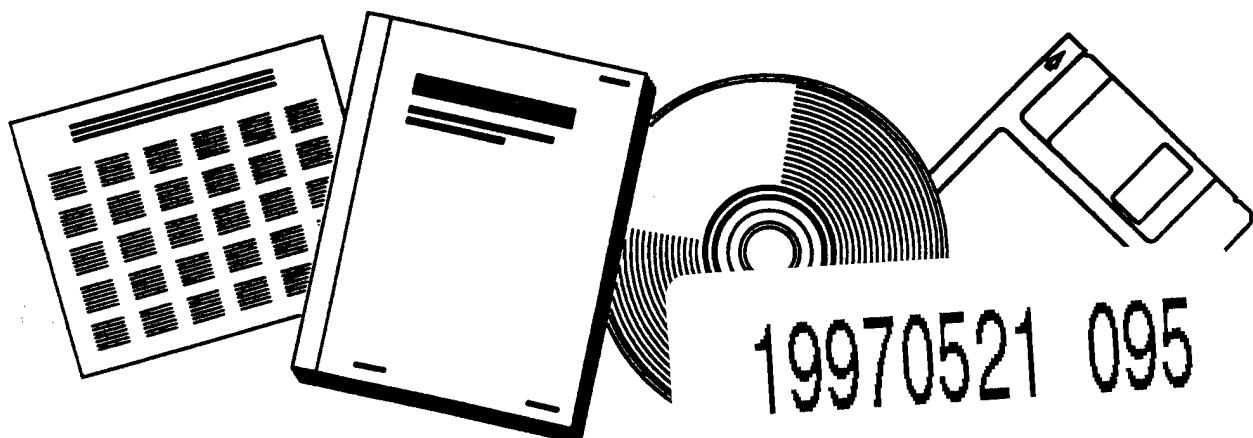
PB93-109973

Chromium Contamination in Army Face Masks

Subcommittee on Chromium Contamination in Army Face Masks
Committee on Toxicology

Board on Environmental Studies and Toxicology
Commission on Life Sciences
National Research Council

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503

PB93-109973

2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
1989	Final

4. TITLE AND SUBTITLE

Chromium Contamination in Army Face Masks

5. FUNDING NUMBERS

Contract No.
DAMD17-89-C-9086

6. AUTHOR(S)

Subcommittee on Chronium Contamination in Army Face Masks

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

National Research Council
2101 Constitution Ave., N.W.
Washington, DC 20418

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Department of the Army

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION AVAILABILITY STATEMENT

Board on Environmental Studies & Toxicology

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The National Research Council's Committee on Toxicology's Subcommittee on Chromium Contamination in Army Face Masks reviewed the possible health risks to soldiers associated with exposure to U.S. Army gas-mask canisters containing activated charcoal impregnated with hexavalent chromium, a carcinogen. The canisters are attached to masks used to detoxify toxic gases, such as hydrogen chloride and cyanogen chloride. In 1982, reports surfaced of dark smudges on the faces of mask users; the smudges were traced to leaking of activated charcoal fines from canisters. The carbon smudging was also associated with some exposure to hexavalent chromium. The subcommittee's review of data provided by the Army on the amounts of chromium released during tests of gas-mask canisters indicated that the amounts of insoluble hexavalent chromium--chromium (VI)--found in the C2 canister (developed by the Canadian Army) and in the field-fixed and redesigned M10A1 canisters are well within the limits implied by standards set by the National Institute for Occupational Safety and Health under worst-case mask use conditions. Although those limits were exceeded for unfixed M10A1 canisters, the lifetime cancer risk even in that case was estimated to be less than 1×10^{-4} under realistic conditions of use. The subcommitt concluded that no special medical followup of military personnel who used M10A1 canisters is needed.

14. SUBJECT TERMS

hexavalent chromium, army face masks, C2 canister, M10A1 canister

15. NUMBER OF PAGES

10

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. 239-18
298-102

Chromium Contamination in Army Face Masks

Subcommittee on Chromium Contamination in Army Face Masks
Committee on Toxicology

Board on Environmental Studies and Toxicology
Commission on Life Sciences
National Research Council

SUBCOMMITTEE ON CHROMIUM CONTAMINATION
IN ARMY FACE MASKS

Bernard M. Wagner, *Chairman,* Nathan S. Kline Research Institute, Orangeburg, New York
William Halperin, National Institute for Occupational Safety and Health, Cincinnati, Ohio
Daniel Krewski, Health and Welfare Canada, Ottawa, Ontario, Canada
Kathleen Taylor, General Motors Research Laboratories, Warren, Michigan
Thomas Tephly, The Toxicological Center, University of Iowa, Iowa City, Iowa

F. William Sunderman, *Adviser,* University of Connecticut, Farmington, Connecticut

Staff

Richard D. Thomas, Project Director
Kulbir S. Bakshi, Program Officer
Marvin A. Schneiderman, Senior Staff Scientist
Erik A. Hobbie, Research Assistant
Norman Grossblatt, Editor
Beulah S. Bresler, Administrative Secretary/Senior Editorial Assistant
Catherine M. Barnes, Administrative Secretary/Senior Program Assistant

COMMITTEE ON TOXICOLOGY

John Doull, *Chairman*, University of Kansas Medical Center, Kansas City, Kansas
Eula Bingham, *Vice-Chairman*, University of Cincinnati, Cincinnati, Ohio
R. Hays Bell, Eastman Kodak Company, Rochester, New York
Charles E. Feigley, University of South Carolina, Columbia, South Carolina
Bruce A. Fowler, University of Maryland, Baltimore, Maryland
Donald E. Gardner, NSI Technology Services Corporation, Research Triangle Park, North Carolina
Mary E. Gaulden, University of Texas, Southwestern Medical School, Dallas, Texas
Walderico Generoso, Oak Ridge National Laboratory, Oak Ridge, Tennessee
Ian Greaves, University of Minnesota, Minneapolis, Minnesota
Rogene F. Henderson, Lovelace Biomedical and Environmental Research Institute, Albuquerque, New Mexico
Nancy Kerkvliet, Oregon State University, Corvallis, Oregon
Carole A. Kimmel, Environmental Protection Agency, Washington, D. C.
Curtis D. Klaassen, University of Kansas Medical Center, Kansas City, Kansas
Ralph L. Kodell, National Center for Toxicological Research, Jefferson, Arkansas
Daniel Krewski, Health and Welfare Canada, Ottawa, Ontario, Canada
Ernest Eugene McConnell, Consultant, Raleigh, North Carolina
I. Glenn Sipes, University of Arizona College of Pharmacy, Tucson, Arizona
Robert Snyder, Rutgers University, Piscataway, New Jersey
Kathleen C. Taylor, General Motors Research Laboratories, Warren, Michigan
Bernard M. Wagner, Nathan S. Kline Research Institute, Orangeburg, New York

Staff

Richard D. Thomas, Program Director
Kulbir S. Bakshi, Program Officer
Robert P. Beliles, Program Officer
Marvin A. Schneiderman, Senior Staff Scientist
Erik A. Hobbie, Research Assistant
Beulah S. Bresler, Administrative Secretary/Senior Editorial Assistant
Catherine M. Barnes, Administrative Secretary/Senior Program Assistant

BOARD ON ENVIRONMENTAL STUDIES AND TOXICOLOGY

COMMISSION ON LIFE SCIENCES

PREFACE

In 1987, a congressional inquiry raised questions regarding the health of soldiers exposed to U.S. Army gas-mask canisters containing activated charcoal impregnated with hexavalent chromium, a carcinogen. The inquiry was prompted by a letter from a constituent asking whether thyroid cancer in the constituent's son could be attributed to Army face-mask use. Although the possibility was considered slight, the Army conducted an internal review and requested review by the Committee on Toxicology (COT) in the National Research Council's Board on Environmental Studies and Toxicology to determine possible health risks associated with face-mask use.

The canisters are attached to the masks used to detoxify inhaled gases, such as hydrogen chloride and cyanogen chloride. Of most concern was the M10A1 canister, used with M24 gas masks by tank crews and with M25 gas masks by aviators. That canister was manufactured in large numbers during World War II. Stocks began to be depleted in the 1970s, and an order was placed with Mine Safety Appliances in 1978 to produce additional M10A1 canisters. In 1982, there were reports of dark smudges on the faces of mask users. The smudges were traced to leaking of activated charcoal fines from the canisters. The carbon smudging was also associated with some exposure to hexavalent chromium, a known carcinogen. To reduce the exposure, a filter-pad insert for the M10A1 canister was developed and put into use in the spring of 1985. The canister with the insert is known as the field-fixed M10A1 canister. A redesigned M10A1 canister to be put into use soon will incorporate the filter pad and thus obviate a field fix.

The charge to COT was to review the data generated on chromium intake from modified and newly developed filter canisters, to assess the potential health effects on soldiers already exposed to leaked chromium, and, if necessary, recommend further studies or remedial actions for the exposed soldiers. COT established the Subcommittee on Chromium Contamination in Army Face Masks to address those issues.

Bernard M. Wagner, M.D.
Chairman
Subcommittee on Chromium Contamination
 in Army Face Masks

John Doull, M.D.
Chairman
Committee on Toxicology

CONTENTS

SUMMARY

The Subcommittee on Chromium Contamination in Army Face Masks of the Committee on Toxicology (COT) in the National Research Council's Board on Environmental Studies and Toxicology of the Commission on Life Sciences reviewed the possible health risks to soldiers associated with exposure to U.S. Army gas-mask canisters containing activated charcoal impregnated with hexavalent chromium, a carcinogen. The canisters are attached to masks used to detoxify toxic gases, such as hydrogen chloride and cyanogen chloride. Of most concern was the M10A1 canister, used with M24 gas masks by tank crews and with M25 gas masks by aviators. In 1982, reports surfaced of dark smudges on the faces of mask users; the smudges were traced to leaking of activated charcoal fines from canisters. The carbon smudging was also associated with some exposure to hexavalent chromium. To reduce the exposure to chromium, the Army developed a filter pad to be inserted into the M10A1 canister. The canister with the insert is known as the field-fixed M10A1 canister. A redesigned M10A1 canister to be put into use soon will incorporate the filter pad and thus obviate a field fix. The Army has tested face-mask canisters to determine whether the amount of chromium that might leak from them poses any health risks.

COT was requested by the Army to:

• Review the data generated on chromium intake from modified and newly developed filter canisters.

• Assess the potential health effects on soldiers already exposed to leaked chromium and, if necessary, recommend further studies or remedial actions for the exposed soldiers.

The subcommittee's review of data provided by the Army on the amounts of chromium released during tests of gas-mask canisters indicated that the amounts of insoluble hexavalent chromium--chromium (VI)--found in the C2 canister (developed by the Canadian Army) and in the field-fixed and redesigned M10A1 canisters are well within the limits implied by standards set by the National Institute for Occupational Safety and Health under worst-case mask use conditions. Although those limits were exceeded for unfixed M10A1 canisters, the lifetime cancer risk even in that case was estimated to be less than 1×10^{-4} under realistic conditions of use. This level of risk has been previously accepted by the Department of Defense (DOD). The subcommittee concluded that no special medical followup of military personnel who used M10A1 canisters is needed.

BACKGROUND

Gas masks use activated charcoal to adsorb toxic gases. As early as the time of World War I, activated charcoal had been impregnated with other substances to improve its ability to trap and destroy toxic gases. At the close of World War I, copper-impregnated charcoal, known as whetlerite, was discovered to be particularly effective in deactivating many gases; the basic process of "whetlerization" is still used. The copper-impregnated charcoal in production in 1940 was derived from whetlerite and designated Type A carbon. The search for more effective gas masks led to activated charcoal impregnated with copper, silver, and chromium salts, which is known as ASC carbon.

The impregnants chemically destroy such agents as phosgene (destroyed by copper), cyanogen chloride (by chromium), and arsine (by silver). Chromium (VI) is a strong oxidant that is particularly effective for the destruction of cyanogen compounds. Chromium prevents penetration of small amounts of cyanogen, which is a by-product of hydrocyanic acid adsorption. Substitution of non-carcinogenic metals--such as zinc, molybdenum, tungsten, and vanadium-- is being considered; efficacy studies of these metals are underway (personal communication, Maurice Weeks). Nerve gases (G agents and VX) and mustard are physically removed by the carbon itself; the metal salts aid in their chemical destruction after adsorption.

Trivalent chromium--chromium (III)--is an essential mineral required for normal glucose metabolism (Mertz, 1969). A chromium intake of 50-200 μg/day for adults has been recommended by the NRC Committee on Dietary Allowances (NRC, 1980), on the basis of long-term studies in humans in which the average dietary intake of 50 μg/day was supplemented with an additional 150 μg/day.

Toxicologic and epidemiologic studies have linked chromium (VI) compounds with the induction of lung cancer (reviewed in IARC, 1980; ATSDR, 1989; U.S. EPA, 1984a,b). At least some of the chromium in the gas-mask canister is in the hexavalent state, so some of the smudge-producing materials leaking from canisters might increase the risk of lung cancer. A search of the literature has not uncovered any reports that chromium is a thyroid carcinogen.

It is impossible to determine precisely how many soldiers used the new (post-1978) M10A1 canisters without the field fix. However, approximately 8,000 M10A1 canisters were requisitioned each month; if unfixed M10A1 canisters were used throughout the period 1982-1985, approximately 400,000 unfixed M10A1 canisters were used. Of that total, 80% (320,000) were for domestic use, and 20% (80,000) were used overseas (primarily in Europe). If domestic personnel changed canisters every 2 yr, overseas personnel changed canisters yearly, and each user was exposed for the full 4 yr (1982-1985), 160,000 domestic personnel and 20,000 overseas personnel were potentially exposed. Turnover in enlistments would imply that more persons were exposed--but to lower cumulative doses.

An interim filter insert and a redesigned M10A1 canister have been developed. A new canister, the C2 canister, was developed by the Canadian Army and is intended for use with the M40 mask, the new general-purpose mask for the U.S. Army.

The Army extensively tested the filter canisters and compared the amounts of chromium released from the canisters with exposure limits established by the American Conference of Governmental Industrial Hygienists (ACGIH), the Occupational Safety and Health Administration (OSHA) of the U.S. Department of Labor, and the National Institute for Occupational Safety and Health (NIOSH) and found them to be below recommended or permissible exposure limits of chromium (VI) (ACGIH, 1986; NIOSH, 1975; U.S. Department of Labor, 1987). Nonetheless, the Army requested an independent expert review by the NRC Committee on Toxicology (COT). The Army's policy has been to attempt to abide by the more stringent of the OSHA and ACGIH standards; the ACGIH standard is the more stringent, at 0.05 mg/m^3. The OSHA standard for soluble chromous and chromic salts is 0.5 mg/m^3 as chromium. However, for the C2 canister and the field-fixed and redesigned M10A1 canisters, the Army Office of the Surgeon General has stipulated that the NIOSH-recommended limit of 1 μg/m^3 (0.001 mg/m^3) be used to minimize potential risk.

CHROMIUM TOXICITY

The subcommittee considered the current toxicologic status of chromium. The major task was to assess the risk of respiratory tract cancer in soldiers exposed to chromium (VI)-containing carbon particles by inhalation when wearing face masks. Other potential health effects are chrome allergies and nonneoplastic lesions of the respiratory tract.

In 1980, the International Agency for Research on Cancer (IARC, 1980) reached the following conclusions regarding carcinogenic risks to humans associated with exposures to chromium compounds:

> There is *sufficient evidence* for the carcinogenicity of calcium chromate and some relatively insoluble chromium (VI) compounds (sintered calcium chromate, lead chromate, strontium chromate, sintered chromium trioxide, and zinc chromate) in rats. There is limited evidence for the carcinogenicity of lead chromate (VI) oxide and cobalt-chromium alloy in rats. The data were inadequate for the evaluation of the carcinogenicity of other chromium (VI) compounds, and of chromium (III) compounds. There is *sufficient evidence* of respiratory carcinogenicity in men occupationally exposed during chromate production. Data on lung cancer risk in other chromium-associated occupations and for cancer at other sites are insufficient. The epidemiologic data do not allow an evaluation of the relative contributions to carcinogenic risk of metallic chromium, chromium (III), and chromium (VI) or of soluble versus insoluble chromium compounds.

IARC came to essentially the same conclusions in 1987, classifying chromium (VI) compounds in group I, indicating sufficient evidence of carcinogenicity, and classifying chromium (III) compounds in group III, indicating inadequate evidence of carcinogenicity (IARC, 1987). The carcinogenic risks associated with chromium compounds were reassessed by an IARC working group in June 1989. Until the working group's report is available, the subcommittee accepts the IARC (1987) judgment as the most reliable available on the carcinogenicity of chromium and chromium compounds.

The major characteristic that affects the metabolism and toxicity of chromium compounds is oxidation state. Cell membranes have low permeability to chromium (III), but are readily penetrated by chromium (VI), which undergoes intracellular reduction to chromium (III). Most chromium (VI) compounds are mutagenic and genotoxic in bacteria and mammalian cells, whereas chromium (III) compounds are typically nonmutagenic in microbial and mammalian test

systems or induce chromosomal aberrations only at very high doses (Hertel, 1985). Chromium (III) derived from intracellular reduction of chromium (VI) can bind to DNA and might represent the ultimate mutagenic form of chromium (Leonard and Lauwerys, 1980).

Chronic exposures of rodents to inhalation of chromate dusts produce inflammatory reactions in the upper and lower respiratory tract (ATSDR, 1989). Lesions of the nose--including mucosal ulceration, perforated septum, and chronic inflammation--have been reported in chrome-platers and other workers exposed to aerosols of chromium (VI) compounds. Chronic pharyngitis, laryngitis, tracheitis, and bronchitis have also been noted in some groups of heavily exposed chromate workers (U.S. EPA, 1984a). Such nonneoplastic disorders of the respiratory tract are unlikely to constitute a substantial problem for soldiers exposed to chromium in face masks at chromium (VI) concentrations below the current NIOSH recommended exposure limits.

When whetlerite dust was instilled intratracheally in rats (Katz, 1986), chromium was deposited mainly in the lungs, kidneys, and liver, which are also the target organs for deposition in humans. Blood, trachea, spleen, and stomach were also examined for chromium. The absence of substantial amounts of chromium from the stomach of the experimental rats indicates that little if any of the instilled dose is removed from the lungs by ciliary action and later swallowed. The absence of chromium from the trachea supports that conclusion. Distribution of the chromium to the body organs and tissues probably begins with transfer from the lungs to the blood. Absorption from the intestine is considered unlikely (Katz, 1986).

The thyroid concentration of chromium has been reported as 430 μg/kg of wet tissue in unexposed subjects and 240-530 μg/kg of wet tissue in chromate workers (IARC, 1980). Those data do not indicate any accumulation of chromium in the thyroid.

Allergic reactions might develop as a result of exposure to chromium in Army face masks. Contact dermatitis and systemic hypersensitivity, including asthma, are among the allergic reactions that have been attributed to chromium in exposed industrial workers (Williams, 1969; U.S. EPA, 1984a; Langard and Norseth, 1986; Moller, 1986). Hence, there is potential risk of contact eczema of facial skin in contact with the masks and of asthmatic attacks in hypersensitive subjects. Pulmonary alveolar macrophages have been identified as cellular targets for chromium toxicity after subchronic, low-level exposures of rats and rabbits to inhalation of chromium (III) and (VI) compounds (Glaser et al., 1985; Johansson et al., 1987). Therefore, the possibility of immunotoxicity due to inhalation of chromium-containing carbon particles, which would presumably be avidly phagocytosed by alveolar macrophages, cannot be dismissed.

Because ASC carbon contains copper, as well as chromium, synergistic toxic effects on joint exposure to these metals are possible. Copper (II) is known to induce free-radical reactions, such as lipid peroxidation (Halliwell and Gutteridge, 1985), and some products of lipid peroxidation might function as promoters of neoplasia (Copeland, 1983).

For greater detail on chromium toxicity, the reader is referred to NRC (1974, 1988); U.S. EPA (1984a,b); and ATSDR (1989).

CHROMIUM STANDARDS

ACGIH (1986) recommends a threshold limit value time-weighted average (TLV-TWA) for water-soluble and water-insoluble chromium (VI) compounds of 0.05 mg/m^3 in air as chromium. ACGIH considered the TLV-TWA of 0.05 mg/m^3 adequate to preclude irritation of the respiratory tract, as well as kidney and liver damage from water-soluble chromic acid and its anhydride and the monochromates and dichromates of sodium, potassium, ammonium, lithium, cesium, and rubidium.

ACGIH includes chromium in its list of known human carcinogens. ACGIH (1986) stated that "there is, unfortunately, little previous environmental data from those exposures associated with increased respiratory cancer risk. With the data available, however, this TLV provides an adequate margin of safety."

OSHA (U.S. Department of Labor, 1987) has set a limit for chromium metal and insoluble salts of 1 mg/m^3 as chromium and a limit for soluble chromous and chromic salts of 0.5 mg/m^3 as chromium.

NIOSH (1975) recommended a permissible exposure limit (PEL) for the carcinogenic chromium (VI) of 1 μg/m^3. That PEL was based on the detection limit for chromium (VI) at the time and the view that exposure to carcinogens should be as low as technology permits.

According to Army computations, the NIOSH-recommended limit of 1 μg/m^3 implies a maximal chromium content of 150 μg/canister. The assumptions used by the Army in that regard are as follows:

• A soldier is exposed to the maximal NIOSH PEL of 1 μg/m^3 every time the canister is worn during its lifetime. (The canister is replaced every 2 yr in the United States and yearly elsewhere.)

• The typical breathing rate of a soldier wearing a mask and canister under (simulated) battlefield conditions is 25 L/min, or 0.025 m^3/min.

• A canister is worn by a soldier for a maximum of 50 h/yr for 2 yr before being replaced with a new canister.

Those assumptions lead to a permissible content of

(1 μg/m^3) (0.025 m^3/min) (60 min/h) (50 h/yr) (2 yr) = 150 μg

of chromium in canisters changed every 2 years, assuming that all the chromium in the canister is released during the period of use. Canisters changed yearly could contain only 75 μg of chromium.

CARCINOGENIC RISK ASSESSMENT

COT has suggested a 24-h emergency exposure guidance level (EEGL) for lithium chromate of 0.05 mg/m^3, corresponding to 0.023 mg/m^3 of chromium (NRC, 1988). That is based on an assessment of the carcinogenic risk associated with chromates; no toxicity data could be found on lithium chromate itself. Those recommendations are not applicable for sustained exposure. However, the exposure of peacetime soldiers to face masks is intermittent and not likely to exceed 50 h/yr, as noted previously.

Epidemiologic data reported by Langård and Norseth (1975) indicated an elevated risk of lung cancer in industrial workers. Based on these data, a 95% upper confidence limit on the lifetime cancer risk of 1 day's (8-h) exposure to chromium at 1 mg/m^3 of inhaled air was determined to be 1.3 x 10^{-4} (NRC, 1988). (That figure assumes that long-term low-level exposures have the same effect as short-term high-level exposures that yield the same total exposure.) For 1 day's exposure at 1 μg/m^3, the cancer risk would be 1.3 x 10^{-7}. For military exposure (at the NIOSH-recommended PEL of 1 μg/m^3) for a maximum of 50 h/yr and for a maximum of 30 yr of military employment, the implied risk would be less than

(1.3 x 10^{-7}/d) (8 h/d)$^{-1}$ (50h/yr) (30 yr) (1.2) = 2.9 x 10^{-5}.

The last factor of 1.2 is included to adjust for the higher breathing rate of soldiers $(0.025 \text{ m}^3/\text{min} \times 60 \text{ min/h} \times 8 \text{ h/d} = 12 \text{ m}^3/\text{d})$ as compared to industrial workers $(10 \text{ m}^3/\text{d})$.

Similar computations based on the laboratory data of Nettesheim et al. (1971) yield a maximal cancer risk for 1 d of exposure at 1.9 mg/m^3 (the average concentration in the animal studies) of 6.3×10^{-6}. For exposure at 1 $\mu\text{g/m}^3$, that implies a risk of

$$(6.3 \times 10^{-6}) \ (0.001 \text{ mg/m}^3) \ (1.9 \text{ mg/m}^3)^{-1} = 3.3 \times 10^{-9}.$$

That is approximately one-fortieth the risk of 1.3×10^{-7} computed from the industrial data.

A lifetime risk of 1×10^{-4} has been considered acceptable for some occupational exposure situations (Travis et al., 1987; Travis and Hettemer-Frey, 1988; International Council on Radiation Protection, 1985), and has been used by DOD in setting emergency exposure guidance levels (EEGLs) for other chemicals with carcinogenic potential (National Research Council, 1988). Since the NIOSH standard of 1 $\mu\text{g/m}^3$ corresponds to an annual exposure of 75 $\mu\text{g/yr}$ and a lifetime risk of 2.9×10^{-5}, the annual exposure leading to a risk of 1×10^{-4} is

$$(75 \ \mu\text{g}) \ (1 \times 10^{-4}/2.9 \times 10^{-5}) = 258.6 \ \mu\text{g}.$$

At that level of risk, each canister could contain approximately 260 μg of chromium if changed yearly or 520 μg of chromium if changed every 2 yr.

The preceding risk analysis corresponds to a worst-case scenario in which a face mask is used for 50 h/yr for 30 yr. The Army has indicated that a more realistic pattern of use is 20 h/yr for up to 8 yr. At that rate,

$$(260 \ \mu\text{g}) \ (50/20) \ (30/8) = 2,438 \ \mu\text{g} \approx 2,400$$

of chromium would be allowed in canisters changed yearly. Canisters changed every 2 yr could contain 4,800 μg of chromium and not exceed a lifetime risk of 1×10^{-4}.

AMOUNTS OF CHROMIUM RELEASED FROM FACE MASKS

The Army Environmental Hygiene Agency (AEHA) conducted a health-hazard assessment of the M10A1 and C2 canisters in 1985 and 1986 and concluded that use of the canisters by military personnel posed no substantial health risk. Only a few canisters were tested. Because of concerns about the reliability and reproducibility of the limited testing, the Under Secretary of the Army in September 1987 directed that a new test program be conducted on the canisters of concern.

The final test protocol developed by the Army was applied by Battelle Corporation, Columbus Division. Five canister groups were tested:

Group 1: 299 M10A1 canisters with filter inserts selected from depot stocks--inserts installed by Chemical Research, Development, and Engineering Center (CRDEC) personnel.

Group 2: 100 M10A1 canisters without filter inserts selected from depot stocks.

Group 3: 100 M10A1 canisters with filter inserts selected from active Army units (inspected by CRDEC).

Group 4: 299 C2 canisters.

Group 5: 1 M14 control canister (containing no chromium), weighed 81 times throughout testing.

In addition, 299 redesigned M10A1 canisters containing factory-installed filters were tested in the spring of 1989; results from that test are not yet available.

The test was designed to extract the maximal amount of carbon dust (hence, chromium) in a short period by subjecting the canister to continuous rapid shaking at high gravitational force (g). Three mechanical testing systems were considered by the Army for dust extraction: the NATO vertical-shock test apparatus, the Berger tester, and the Canadian horizontal-shaker test apparatus (Q261). The method used by the contractor was based on the shake test developed by the Canadian government to determine maximal contamination of its C2 canister. The Canadian apparatus was selected, because the g forces developed during the test corresponded to those for a soldier in the field under worst-case conditions. The Canadian test gave average g forces in the x, y, and z coordinates of 20, 6, and 6.5 g, respectively, to be compared with the time-weighted averages of human-use testing of 2.1, 2.5, and 2.7 g for normal-use conditions and 3.4, 4.1, and 4.4 g for worst-case conditions. It is the opinion of the Army that the higher g levels obtained with the Canadian test yielded a sufficient margin of safety for use of the test data. In the Canadian test, the canister is shaken 400 times/min.

The standard operating procedure used by Battelle involved quality-control checks at all stages, from the calibration of the air-flow meter to the final determination of chromium. The basic test procedure is simple: A canister is loaded onto the Q261 apparatus in an upright position to maximize dust extraction and connected to a filter. Air is drawn through the canister and filter at an average rate of 45 L/min for 20 min as the canister is shaken. The filter, which has collected loose particles from the canister, is analyzed for carbon dust and chromium. No attempt is made to determine the proportions of chromium of different valence states. For purposes of safety evaluation, all the chromium collected is assumed to be hexavalent and carcinogenic.

The shake-test results are not direct measures of human exposure. No reliable human-exposure data on personnel wearing masks are available, so no direct correlation can be made between human risk and shake-test results. However, the shake test does provide some indication of maximal exposure. Analyses are based on the assumption that a user of a canister would be exposed to all the chromium and carbon in the canister during its useful lifetime.

Care was taken to ensure "blind" conditions for testing the canisters and for analysis for carbon dust and chromium. Canisters were identified solely by code numbers, to ensure that personnel never knew which type of canister was being tested. The sequence of testing of all the canisters except the standard, unfixed M10A1 was random. Because of problems with contamination of the testing environment, the 100 unfixed M10A1 canisters (Group 2) were tested as a single block.

The Army Materiel Systems Analysis Activity (AMSAA) examination of the results obtained by Battelle in the shake tests (Table 1) (Edwards, 1989) showed that none of the M10A1 canisters with the filter or C2 canisters (Groups 1, 3, and 4) exceeded the limits of 75 or 150 μg for canisters changed every 1 or 2 yr, respectively. Observations of canisters containing less chromium than the detection limit of 0.01 μg were considered "censored" observations. Of the 100 M10A1 canisters without filter inserts (Group 2), 55 exceeded the 2-yr limit of 150 μg of chromium; the highest amount reported was 4,290 μg.

The M14 canister was used to monitor whether outside factors affected results. The apparent finding of chromium indicates a contamination problem, probably arising from the laboratory atmosphere. Thus, values for the C2 canisters (Group 4) and redesigned and field-fixed M10A1 canisters (Groups 1 and 3) are likely to be overestimates.

TABLE 1

SUMMARY OF SHAKE-TEST CHROMIUM DATA[a]

Canister Group	No. Canisters	No. Censored Observations	Chromium Extracted Per Canister, µg			
			Average	Standard Deviation	Min.[b]	Max.
1 (M10A1, redesigned)	299	45	0.36	0.84	nd	6.70
2 (M10A1, without insert)	100	0	520	752	1.31	4,290
3 (M10A1, with insert, from active units)	100	16	0.44	1.80	nd	11.30
4 (C2 canisters)	299	5	1.56	1.82	nd	14.50
5 (M14, control)	81[c]	10	0.68	1.54	nd	7.88

[a]Data from Edwards (1989).
[b]nd = not detectable (canisters containing less chromium than the detection limit of 0.01 µg).
[c]One M14 canister--always the same canister--that contained no chromium was tested as a negative control 81 times.

CONCLUSIONS

1. Results of analyses of chromium release during shake tests of ASC carbon canisters with filter inserts indicate that inhalation exposure of soldiers to insoluble chromium (VI) compounds is well below the current standards or recommendations for the workplace, and the canisters are thus deemed acceptable for military use. In particular, the amounts of chromium found in the C2 canisters and the field-fixed and redesigned M10A1 canisters are much lower than the limit of 75-150 µg implied by the NIOSH standard for chromium under worst-case scenarios of mask use.

2. The worst-case exposure assumption (30 yr of mask use at 50 h/yr) implies that exposure to canisters containing 520 µg of chromium and replaced every 2 yr would lead to a lifetime risk of lung cancer of 1×10^{-4}, a risk level previously accepted by DOD. For a more realistic pattern (up to 8 yr at 20 h/yr) of exposure to canisters containing as much as 4,800 µg of chromium would still be expected to lead to a lifetime risk of 1×10^{-4} or less. The average amount of chromium in M10A1 canisters was 520 µg, with a maximum of 4,290 µg.

3. No evidence has been found that links exposure to chromium in any form to thyroid cancer.

4. Considering the likely conditions of exposure, no special medical followup of military personnel who used unfixed M10A1 canisters appears to be needed.

8

REFERENCES

ACGIH (American Conference of Governmental Industrial Hygienists). 1986. Chromium. Pp. 139—140 in Documentation of the Threshold Limit Values and Biological Exposure Indices, 5th ed. Cincinnati, Ohio: American Conference of Governmental Industrial Hygienists, Inc.

ATSDR (Agency for Toxic Substances and Disease Registry). 1989. Toxicological Profile for Chromium. U.S. Public Health Service and U.S. Environmental Protection Agency. 135 pp.

Copeland, E.S. 1983. A National Institutes of Health Workshop Report. Free radicals in promotion: A chemical pathology study section workshop. Cancer Res. 43:5631—5637.

Edwards, K. 1989. The Evaluation of a Chromium and Carbon Dust Emission Test for the M10A1 and C2 Chemical Protective Canisters. Reliability, Availability and Maintainability Division. U.S. Army Materiel Systems Analysis Activity, Aberdeen Proving Ground, Md.

Glaser, U., D. Hochrainer, H. Klöppel, and H. Kuhnen. 1985. Low level chromium (VI) inhalation effects on alveolar macrophages and immune functions in Wistar rats. Arch. Toxicol. 57:250—256.

Halliwell, B., and J.M.C. Gutteridge. 1985. Free Radicals in Biology and Medicine. Oxford: Clarendon Press. 346 pp.

Hertel, R.F. 1985. Sources of exposure and biological effects of chromium. Pp. 63—77 in Environmental Carcinogens: Selected Methods of Analysis, Vol. 8. I. K. O'Neill, P. Schuller, and L. Fishbein, eds. Lyon, France: International Agency for Research on Cancer.

IARC (International Agency for Research on Cancer). 1980. Chromium and chromium compounds. Pp. 205—323 in IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans: Some Metals and Metallic Compounds, Vol. 23. Lyon, France: International Agency for Research on Cancer.

IARC (International Agency for Research on Cancer). 1987. Pp. 165—168 in IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Supplement 7. Lyon, France: International Agency for Research on Cancer.

International Council on Radiation Protection. 1985. Quantitative Bases for Developing a Unified Index of Harm. Publication No. 45. Oxford, England: Pergamon Press.

Johansson, A., B. Robertson, T. Curstedt, and P. Camner. 1987. Alveolar macrophage abnormalities in rabbits exposed to low concentrations of trivalent chromium. Environ. Res. 44:279—293.

Katz, S.A. 1986. The Bioavailability and Systemic Distribution of Chromium from Whetlerite in the Rat. Aberdeen Proving Ground, Md.: Toxicology Division, Chemical Research, Development and Engineering Center. U.S. Army Armament Munitions Chemical Command. Contract No. DAAG29-81-D-0100.

Langård, S., and T. Norseth. 1975. A cohort study of bronchial carcinomas in workers producing chromate pigments. Br. J. Ind. Med. 32:62—65.

Langård, S., and T. Norseth. 1986. Chromium. Pp. 185—210 in Handbook on the Toxicology of Metals, L. Friberg, G. F. Nordberg, and V. B. Vouk, eds. Amsterdam: Elsevier.

Leonard, A., and R.R. Lauwerys. 1980. Carcinogenicity and mutagenicity of chromium. Mutat. Res. 76:227—239.

Mertz, W. 1969. Chromium occurrence and function in biological systems. Physiol. Rev. 49:163—239.

Moller, D.R., S.M. Brooks, D.I. Bernstein, K. Cassedy, M. Enrione, and I.L. Bernstein. 1986. Delayed anaphylactoid reaction in a worker exposed to chromium. J. Allergy Clin. Immunol. 77:451—456.

Nettesheim, P., M.G. Hanna, Jr., D.G. Doherty, R.F. Newell, and A. Hellman. 1971. Effect of calcium chromate dust, influenza virus, and 100 R whole-body X radiation on lung tumor incidence in mice. J. Nat. Cancer Inst. 47:1129—1144.

NIOSH (National Institute for Occupational Safety and Health). 1975. Criteria for a Recommended Standard: Occupational Exposure to Chromium (VI). HEW Publication No. (NIOSH) 76-129. Washington, D.C.: U.S. Department of Health, Education, and Welfare.

NRC (National Research Council). 1974. Medical and Biologic Effects of Environmental Pollutants: Chromium. Washington, D.C.: National Academy Press. 155 pp.

NRC (National Research Council). 1980. Recommended Dietary Allowances. 9th Ed. Washington, D.C.: National Academy Press. 185 pp.

NRC (National Research Council). 1988. Emergency and Continuous Exposure Guidance Levels for Selected Airborne Contaminants, Vol. 8: Lithium Chromate and Trichloroethylene. Washington, D.C.: National Academy Press. 65 pp.

Travis, C.C., and H.A. Hattemer-Frey. 1988. Determining an acceptable level of risk. Environ. Sci. Technol. 22:873—876.

Travis, C.C., S.A. Richter, E.A.C. Crouch, R. Wilson, and E.D. Klema. 1987. Cancer risk management. Environ. Sci. Technol. 21:415—420.

U.S. Department of Labor. 1987. Occupational Safety and Health Standards: Toxic and Hazardous Substances. Code of Federal Regulations Title 29, Sec. 1910—1000.

U.S. EPA (U.S. Environmental Protection Agency). 1984a. Health Assessment Document for Chromium. Final Report. EPA-600/8-83-014F. NTIS PB85-115905. Research Triangle Park, N.C.: U.S. Environmental Protection Agency.

U.S. EPA (U.S. Environmental Protection Agency). 1984b. Health Assessment for Hexavalent Chromium. EPA/540/1-86/019. NTIS PB86-134301. Cincinnati, Ohio: U.S. Environmental Protection Agency. 37 pp.

Williams, C.D. 1969. Asthma related to chromium compounds. Report of two cases and review of the literature on chromate diseases. N.C. Med. J. 30:482.

U.S. DEPARTMENT OF COMMERCE
Technology Administration
National Technical Information Service
Springfield, VA 22161   (703) 487-4650

PB93109973

BA

BIN: M53   05-09-97
INVOICE: 430223
SHIPTO: 1*89997
PAYMENT: CSH*CPDAG